an absolute insulator again after a few hours. There is possibly some connexion between this alteration of resistance of thin films and the photo-electric fatigue mentioned by Allen, and some experiments are being made at present to test it.

I have great pleasure in recording my best thanks to Professor Stroud, of the Armstrong College, Newcastle-on-Tyne, and to Professor W. M. Hicks, of the University of Sheffield, for the use of the apparatus necessary for the above experiments.

XXIII. *The Electron Theory of Contact Electromotive Force and Thermoelectricity.* By O. W. RICHARDSON, *Professor of Physics, Princeton University* *.

THE following method of deducing certain formulæ which connect some of the physical properties of conductors, particularly in the domain of thermoelectricity, with the number and state of the free electrons present in them, is a natural development of considerations which the writer put forward some time ago in order to account for the laws which regulate the emission of negative electrons from hot bodies †. The method is based on two fundamental assumptions. The first, which is common to all forms of the electron theory of metallic conduction, is that the electric current in metals is carried by electrons which move about freely, exert a pressure, and are otherwise dynamically equivalent to the molecules of a gas. The second is that the potential energy of an electron is much less when it is inside an uncharged conductor than when it is extracted and removed to a considerable distance. It follows that a definite amount of work w has to be done by an electron before it can escape from a conductor, and it is the force at the interface, which corresponds to this amount of work, which retains the electrons in the conductor at ordinary temperatures.

This position has recently been strengthened by an accumulation of experimental evidence. It has been found to give an adequate quantitative explanation of the number of electrons emitted by hot bodies under different conditions. The emitted electrons have been found to have a distribution of velocity in accordance with the requirements of Maxwell's law, and to have a mean translatory kinetic energy identical

* Communicated by the Author.

† *Camb. Phil. Proc.* vol. xi, p. 286 (1901); *Phil. Trans. A.* vol. cci, p. 497 (1903).

with that of a molecule of a gas at the temperature of the metal. By an application of the principles of the kinetic theory of gases it follows that the same statements are true of the free electrons *inside* the metal at the same temperature. Finally, the existence of the work w has been put on a firm basis by the discovery of the corresponding heating and cooling effects when electrons pass into and out of a metal.

Several of the calculations which follow have been given by the writer in a course of lectures on the electron theory of matter, in the past few years. It seems desirable to publish them apart as the results which have been obtained by other investigators in this subject are not in complete accordance, and a discussion of the differences sheds some light on the nature of the phenomena concerned. The strength of the present method lies in the fact that it is completely independent of the idea of free paths, and of the assumptions about the nature of collisions which play a prominent part in most forms of the electronic theory of conductors.

We shall suppose that all the free electrons are alike and negatively charged in order to simplify the calculations; although the method is equally applicable to the case in which different kinds of electrons, both positive and negative, are considered to be present. The view that there are several kinds of free electrons to be reckoned with can hardly be considered to have had much success so far in reducing the apparently rather considerable inconsistencies of the electron theory of conduction. In what follows very considerable use will be made of the theorem that in any system in equilibrium at a constant temperature θ , if n_1 is the concentration of the electrons at a point A and n_2 that at a point B then

$$\frac{n_2}{n_1} = e^{-W/R\theta},$$

where W is the work done in taking an electron from A to B and R is the gas constant in the equation $pv = R\theta$, reckoned for a single electron. This theorem* has been proved by writers on the kinetic theory of matter with a degree of generality which covers all the conditions contemplated in the electron theory of conductors.

We shall suppose each metal to be characterized by the possession of a number n of free electrons per unit volume. The value of n is different for different metals, and for a given metal it is a function of the temperature θ only. In

* Cf. Jeans, 'Dynamical Theory of Gases,' p. 78.

every case n is a very large number, so large that the fractional change in n produced by the communication of an electrostatic charge to a conductor of finite size is negligible in all practical cases. The largeness of n is of course deduced from the results of experiments interpreted by the light of the electron theory. The functions w which measure the work done by an electron in passing from the interior to the exterior of a conductor are also to be regarded as characteristic of each substance. They are functions of the temperature both explicitly and implicitly through n .

Intrinsic Potential Differences.

We shall begin by considering a vacuous enclosure surrounded by insulating walls maintained at a constant temperature θ . We shall also suppose that the thermionic emissivity of the material bounding the enclosure is so small that it may be disregarded. If an initially uncharged metallic conductor is placed inside such an enclosure it will emit negative electrons, the initial rate of emission being much greater the higher the temperature of the metal. Clearly this process will not go on indefinitely. The positive charge which the metal acquires, in virtue of the emission, tends to pull the electrons back, and ultimately a steady state is reached in which as many return as are emitted in a given time. This steady state will be accompanied by a statistically steady distribution of the external electrons, and also of the external electric potential. The theorem which we have already mentioned enables us at once to write down the relation between the concentration of the electrons n and n' at any two external points whose potentials are V and V' . It is

$$\frac{n}{n'} = e^{-\frac{\epsilon(V-V')}{R\theta}},$$

where ϵ is the charge on an electron. Since there is equilibrium between the electrons inside and outside the conductor we have further

$$\frac{n}{n_1} = e^{-\{w_1 + \epsilon(V - V_1)\} R/\theta},$$

where n and V correspond to any external point, as before, n_1 is the number of free electrons per cub.centim. inside the metal, V_1 is the potential at its surface, and w_1 is the work done by an electron in crossing the surface of the conductor from the interior.

Now suppose that there are two conductors of different materials present in the enclosure. As in the previous case, they are to be of considerable size, so that the electrons which they emit are small in number compared with those which are retained. For the present we shall also suppose that the two bodies are not in contact with each other. As before, the electrons in the two conductors and in the surrounding enclosure will ultimately reach a condition of statistical equilibrium, and the conductors will acquire definite potentials, which we may denote by V_1 and V_2 . Let W be the work done in taking an electron from the first to the second conductor when equilibrium has been established. Then

$$\frac{n_2}{n_1} = e^{-W/R\theta},$$

or

$$W = R\theta \log \frac{n_1}{n_2}.$$

But this work is also equal to

$$w_1 + \epsilon(V_2 - V_1) - w_2,$$

where the suffixes refer to the values of the different quantities for the two conductors. Hence

$$w_1 - \epsilon V_1 - R\theta \log n_1 = w_2 - \epsilon V_2 - R\theta \log n_2.$$

Similarly, if there are r conductors,

$$\begin{aligned} w_1 - \epsilon V_1 - R\theta \log n_1 &= w_2 - \epsilon V_2 - R\theta \log n_2 \\ &= \dots = w_r - \epsilon V_r - R\theta \log n_r. \end{aligned}$$

Thus the final state of equilibrium is characterized by the invariance of $w - \epsilon V - R\theta \log n$. This holds both for the internal and the external electrons, since $w=0$ for the latter.

The steady difference of potential $V_m - V_q$ between any two conductors m and q is evidently

$$V_m - V_q = \frac{1}{\epsilon} \left\{ w_m - w_q + R\theta \log \frac{n_q}{n_m} \right\}.$$

So far we have supposed all the bodies to be separate from each other, but the results are equally true if any number of them are in contact. To prove this it is necessary to consider the conditions which determine the state of equilibrium of the system more fully than we have done. Disregarding the electrons present in the surrounding space, which may be done here on account of the smallness of the external

pressures, it is evident that the state of the system is completely determined by the n variables $w_1 w_2 \dots w_n$, the n variables $n_1 n_2 \dots n_n$, and $n-1$ of the variables $V_1 V_2 \dots V_n$, one of which is arbitrary, together with the temperature θ . Now the $n-1$ equations of the type

$$w_m - \epsilon V_m - R\theta \log n_m = w_p - \epsilon V_p - R\theta \log n_p$$

are not the only equations connecting the $3n-1$ variables. We have seen that the w 's are functions of the n 's and θ , so that there are n equations of the type $w_p = f_p(n_p, \theta)$. In virtue of the equilibrium between the negative electrons and the positive remainder inside each conductor there are also n equations of the type $n_p = F_p(\theta)$. There are thus $3n$ variables and $3n-1$ equations, so that when θ is given all the n 's and w 's and the differences $V_m - V_q$ are determined. This is true independently of the relative position of the different conductors, and includes physical and electrical contact as a particular case. It is clear that

$$V_m - V_p = \frac{1}{\epsilon} \left\{ w_m - w_p + R\theta \log \frac{n_p}{n_m} \right\}$$

measures a true intrinsic difference of potential (contact electromotive force) between the conductors m and p .

The values of the electrical conductivity and some other considerations indicate that the number n of free electrons in unit volume is of the same order of magnitude for all the

metallic conductors, and the term $R\theta \log \frac{n_p}{n_m}$ is found to lead

to comparatively small electromotive forces of the order of magnitude of those required to account for the Peltier effect. So far no method has been devised for measuring the values of the w 's except at high temperatures, and the relation between any given w and the temperature is a matter of much uncertainty, so it is rather risky to argue from the values of the w 's at high temperatures to the values of these functions at ordinary temperatures. Broadly speaking, however, there is no doubt that the more electropositive metals have smaller values of w , and the differences which have actually been observed are of the order of magnitude which corresponds to the Volta effect. The fact that negative electrons are emitted at much lower temperatures from the alkali metals than from their more electronegative brethren strongly supports this view, since the concentration of the free electrons is much the same in all cases. It seems to

the writer that the balance of the evidence is now strongly in favour of the view that the Volta contact electromotive force is an intrinsic property of the pure metals, and not, as is perhaps more widely believed, an accidental development caused by traces of chemical action. At the same time there is no reason for doubting that the actual measured value of the contact electromotive force is very sensitive to actions of a chemical nature, as it should be on the view we have been discussing.

The case for the chemical origin of contact electromotive force rests largely on the results of a number of experiments which show that under certain circumstances, which are usually interpreted as involving the absence of oxygen or water-vapour from the surface films, the contact electromotive force, as measured by the condensing electroscope or an equivalent method, is found to either vanish or drop to a comparatively small value. The circumstances referred to are rather varied, and include boiling in heavy oil at about 140°C . (J. Brown *), exposure to the temperature of liquid air (Majorana †), and heating in a vacuum in the presence of drying agents (Spiers ‡, Greinacher §). In all these cases it seems quite likely that the surface of the metals under examination becomes covered with an insulating layer which entangles the escaping electrons. This would give rise to a double layer at the surface of each metal, and the seat of the whole of the potential difference between the metals would lie in these double layers. The surface of each metal would then act like a condenser positively charged on the metal side and negatively on the other. On separating the plates there would be no change in the capacity of the system and no free charges would be developed. An explanation along similar lines accounts for the null effects obtained by Greinacher by the ionization method. It seems quite clear that when the plates are immersed in insulating oil the apparent contact difference of potential will vanish on the electron theory. In the case of Majorana's experiment it is necessary to suppose either that a minute film of condensed moisture develops on the plates, or that the hydroxide films always present become non-conducting at the low temperatures. In any case a film a few molecules in thickness is all that is required. It is significant that Greinacher using the ionization method was unable to confirm Majorana's result. In

* *Phil. Mag.* [5] vol. v. p. 591 (1903).

† *Atti de Lincei*, vol. ix. p. 162 (1900).

‡ *Phil. Mag.* [4] vol. xlix. p. 70 (1900).

§ *Ann. der Physik*, vol. xvi. p. 708 (1906).

the cases in which the surface-films of gas are removed by heating it is to be expected that the oxide films which remain will be non-conducting, and this attitude is definitely supported by the fact that Greinacher was unable to get rid of the contact electromotive force by any kind of treatment when one of the metals tested was platinum, which is notoriously difficult to oxidize.

When two of the metals are joined by an electrolyte there will be no true equilibrium until the battery thus formed has run down, so that the potentials of the metals in the enclosure will not be the same as those they possess in the steady state. The present point of view does not, in fact, affect the thermodynamic theory of electrolytic cells, according to which their electromotive forces are determined by the heat generated by the chemical actions involved.

The Peltier Effect.

We shall now return to the case of two metals in contact. Consider the work done in taking an electron from one to the other in two ways: first, through the junction, and second, by crossing the outer surfaces. We thus obtain two equivalent expressions for the work P per unit charge, viz.

$$P = \frac{w_1 - w_2}{e} + V_2 - V_1 = \frac{R\theta}{e} \log \frac{n_1}{n_2}.$$

The second formula agrees with that given by J. J. Thomson* for the Peltier effect, but differs by a factor of two from the corresponding expression found by Drude†. Thomson's calculation is based on the idea that the electrons are in equilibrium under the opposing action of the electric force and the pressure gradient at the boundary, whereas Drude supposes a kind of convective equilibrium between the diffusion of the ions arising from the varying concentration and the electric currents arising from the balancing difference of potential. It seems to the writer that the standpoint taken by Thomson is much the safer of the two.

It does not seem quite certain, without further consideration, that the expression $\frac{R\theta}{e} \log \frac{n_1}{n_2}$ will represent the heating effect due to the passage of an electric current across the junction of two dissimilar metals, as the energy might conceivably be changed, partly or entirely, into some form other than heat. The fact may, however, be established by the

* 'Corpuscular Theory of Matter,' p. 74.

† *Ann. der Physik*, vol. i. p. 590 (1900).

following thermodynamic argument. Suppose that we have an electrical circuit made up of two metals A and B, such that the parts A and B with the junction J are maintained at the constant temperature θ , and A' and B' are at the constant

temperature θ' . The connexions between A A' B' and B may be imagined as being made by conductors of small cross-section protected by insulating covering when necessary for the argument. The connexions are removable when required, and the magnitude of the conductors A A' B' and B is supposed to be indefinitely large. Each conductor is surrounded by an insulating surface which does not absorb the electrons contained within it. A reversible cycle may be carried out by evaporating some definite quantity, let us say one gram molecule, of the electrons from A, condensing them at A', making them pass through the junction J' to B', evaporating at the surface of B', condensing at B, and returning through the junction J to A. In order to be sure that the cycle is reversible it is necessary to be careful about the way in which the electrons are transferred from A to A' and from B' to B. Of course as the different parts of the system are at different temperatures the state of each conductor will never be exactly that corresponding to thermal equilibrium at the specified temperature, but it may be made to approach that state with any desired degree of approximation by increasing the size of A A' B' and B in comparison with that of their connexions and the enclosure, the temperatures being maintained by contact over indefinitely large areas with electrical insulators kept at the specified temperatures. Under these circumstances the conductors will assume values of w , n , and

V which differ by indefinitely small amounts from the true equilibrium values at the specified temperatures. Thus in general the pressure p_1 , the temperature θ , and the electric potential V_1 of the electrons in equilibrium with A will all be different from the corresponding quantities θ' , p_1' , and V_1' of the electrons in equilibrium with A'. Let us suppose that $\epsilon V_1'$ is $> \epsilon V_1$. Around A place a screen (wire gauze) maintained at the potential V_1' and permeable to the electrons. This will reduce the pressure of the electrons outside of it to some definite value p_1^0 without affecting their temperature θ^* , and will reduce their potential to the value V_1' of the electrons in equilibrium with A'. The further transference of the electrons to A' will not involve any work against the electrical forces, and may be calculated on the hypothesis that the electrons are dynamically equivalent to a perfect gas †. The work done during the evaporation through the potential screen is $pv = NR\theta$ and the heat absorbed is

$$N(w_1 + \epsilon(V_1' - V_1) + R\theta),$$

where N is the number of electrons in one gram-molecule of them.

The freed electrons are then compressed adiabatically to a temperature θ' , the work done in this operation being $\frac{NR}{1-\gamma}(\theta' - \theta)$, where γ is the ratio of the specific heats of the electrons at constant pressure and constant volume. The heat absorbed in this operation is zero, but the pressure is changed from p_1^0 to $p_1^0 \left(\frac{\theta}{\theta'}\right)^{\gamma/\gamma-1}$. We next expand to the pressure p_1' at constant temperature θ' . The work done is $-NR\theta' \log \frac{p_1'}{p_1^0} \left(\frac{\theta}{\theta'}\right)^{\gamma/\gamma-1}$, and an equal amount of heat is absorbed. The electrons now have the same pressure, temperature, and potential as those in equilibrium with A', and the transference has been accomplished in a strictly reversible manner. They are then condensed into A', which is for the time being disconnected from the other conductors, at the constant pressure p_1' and temperature θ' . The work done in this operation is $-NR\theta'$ and the heat absorbed is $-N(w_1' + R\theta')$. The transference from A' to B' involves no work, but there is an amount of heat $-NP'e$ absorbed at the junction, where P' is the Peltier effect per unit charge. The electrons are then evaporated from B' at the equilibrium

* Cf. O. W. Richardson, Phil. Mag. [5] vol. xviii. p. 695 (1909).

† See below, p. 273.

pressure and temperature p_2' and θ' respectively, the work being $NR\theta'$ and the absorption of heat $N(w_2' + R\theta')^*$.

Next compress adiabatically to θ . The work is $\frac{NR}{1-\gamma}(\theta - \theta')$, the heat absorbed being nil. During this step the pressure is changed from p_2' to $p_2' \left(\frac{\theta'}{\theta}\right)^{\gamma/1-\gamma}$. Next expand at constant temperature θ to the pressure p_2^0 , which is the equilibrium pressure at the potential screen around the conductor B. [We have assumed, for the sake of definiteness, that $\epsilon V_2' > \epsilon V_2$.] The work done and heat absorbed in this step are each equal to $-NR\theta \log \frac{p_2^0}{p_2'} \left(\frac{\theta}{\theta'}\right)^{\gamma/1-\gamma}$. Now condense into B at θ and p_2^0 . The work is $-NR\theta$ and the heat absorbed is $-N(w_2 + \epsilon(V_2' - V_2) + R\theta)$. Finally, pass through the junction to A. The work here is nil, and the absorption of heat is $NP\epsilon$. The system is now in the state in which we found it, and the cycle of operations is reversible at every point.

The balance of work done during the cycle is

$$NR\theta' \log \frac{p_1^0}{p_1'} \left(\frac{\theta}{\theta'}\right)^{\gamma/1-\gamma} - NR\theta \log \frac{p_2^0}{p_2'} \left(\frac{\theta}{\theta'}\right)^{\gamma/1-\gamma}.$$

The heat communicated to the source is

$$N\{R\theta \log \frac{p_2^0}{p_2'} \left(\frac{\theta}{\theta'}\right)^{\gamma/1-\gamma} + w_2 - w_1 + \epsilon(V_1 - V_1' + V_2' - V_2) - P\epsilon\}.$$

The ratio of these is equal, by the second law of thermodynamics, to $\frac{\theta' - \theta}{\theta}$; whence by virtue of the relations

$$R\theta \log p_1^0 = R\theta \log P_1 - w_1 - \epsilon(V_1' - V_1),$$

$$R\theta' \log p_1' = R\theta' \log P_1' - w_1',$$

$$R\theta \log p_2^0 = R\theta \log P_2 - w_2 - \epsilon(V_2' - V_2),$$

$$R\theta' \log p_2' = R\theta' \log P_2' - w_2',$$

$$R\theta' \log P_2' = R\theta' \log P_1' + w_2' - w_1' + \epsilon(V_1' - V_2'),$$

$$R\theta \log P_2 = R\theta \log P_1 + w_2 - w_1 + \epsilon(V_1 - V_2),$$

which determine the equilibrium between the electrons in the different parts of the system which are at the same

* When the nomenclature is not quite clear from the context it will be obvious after a glance at the diagram (p. 270).

temperature, if P_1 , P_1' , P_2 and P_2' are the pressures of the free electrons inside A , A' , B and B' , we find that

$$P\epsilon = R\theta \log \frac{P_2}{P_1},$$

showing that this expression or its equivalent $R\theta \log \frac{n_2}{n_1}$ is the true value of the cooling effect at the junction.

The Legitimacy of Applying the Gas Equation.

Objection to the results of the foregoing discussion may be urged on the score of the propriety of applying the equation of a perfect gas $pv = NR\theta$ to the electrons. At any rate the legitimacy of the application is not obvious without further consideration. It might be thought, for instance, that the pressure arising from the mutual repulsion of the electrons would seriously modify the simple equation, and that corrections would have to be introduced somewhat after the manner of Van der Waals's treatment of a real gas. It will be noticed, however, that the equation $pv = R\theta$ has only been applied to the external electrons, and the concentration of these is always exceedingly small at moderate temperatures. Now the correction for the work done by the mutual repulsion of the electrons depends upon the square of the concentration, and thus vanishes, in comparison with the external work, in the limit when the concentration is small. On the other hand, the size of the electrons is very much less than that of a molecule, so that the correction for the finite size of the particles will be infinitesimal. It seems, therefore, that at small concentrations a collection of electrons will exhibit a closer dynamical approximation to the ideal gas than will any real gas under comparable conditions.

The Thomson Effect.

The expression for Lord Kelvin's specific heat of electricity may be deduced by means of a thermodynamic cycle, similar to that already considered, but not quite so complicated. It is now necessary to consider only two conductors, A and A' , of the same material but with different temperatures, θ and θ' . They are joined by a thin conductor of the same material, down which there is, of course, a constant stream of heat. Let the potential outside A be V_1 and that outside A' V_1' , and let $\epsilon V_1'$ be $> \epsilon V_1$. As before we surround A by a potential filter maintained at V_1' . The reversible cycle consists in evaporating the electrons from A through the potential filter, bringing them by reversible processes to the

same temperature and pressure as those outside B, condensing them at B, and allowing them to flow down the conductor back to A.

In evaporating from A the work done is $NR\theta$, and the heat absorbed is $N(w_1 + \epsilon(V_1' - V_1) + R\theta)$. The work during the adiabatic transformation from θ to θ' is $\frac{NR}{1-\gamma}(\theta' - \theta)$, the heat absorbed nil, and the pressure changes from p_1^0 to $p_1^0 \left(\frac{\theta}{\theta'}\right)^{\gamma/1-\gamma}$. The next step consists in expanding to the pressure p_1' at the constant temperature θ' . The work done here is $-NR\theta' \log \frac{p_1'}{p_1^0} \left(\frac{\theta}{\theta'}\right)^{\gamma/\gamma-1}$, and an equal amount of heat is absorbed. In condensing into A' at constant temperature θ' and pressure p_1' the work is $-NR\theta'$ and the heat absorbed $-N(w_1' + R\theta')$. The flow down the conductor from A' to A is not accompanied by the expenditure of work, but involves an absorption of heat

$$= +N\epsilon \int_{\theta'}^{\theta} \sigma d\theta,$$

where σ is the specific heat of electricity.

Applying the second law of thermodynamics in the form

$\int \frac{dQ}{\theta} = 0$, we have, for the entire reversible cycle,

$$\frac{N(w_1 + \epsilon(V_1' - V_1) + R\theta)}{\theta} - \frac{NR\theta' \log \frac{p_1'}{p_1^0} \left(\frac{\theta}{\theta'}\right)^{\gamma/\gamma-1}}{\theta'} - \frac{N(w_1' + R\theta')}{\theta'} + N\epsilon \int_{\theta'}^{\theta} \frac{\sigma}{\theta} d\theta = 0,$$

and since

$$R\theta \log p_1^0 = R\theta \log P_1 - w_1 - \epsilon(V_1' - V_1),$$

and

$$R\theta' \log p_1' = R\theta' \log P_1' - w_1',$$

we have

$$+ \epsilon \int_{\theta'}^{\theta} \frac{\sigma}{\theta} d\theta - R \log \frac{P_1'}{P_1} - \frac{R\gamma}{\gamma-1} \log \frac{\theta}{\theta'} = 0,$$

whence by differentiation with respect to θ

$$\sigma = + \frac{1}{\epsilon} \left\{ \frac{R\gamma}{\gamma-1} - R\theta \frac{\partial}{\partial \theta} \left(\log \frac{P_1'}{P_1} \right) \right\}$$

if P is the pressure of the internal free electrons at the point whose temperature is θ and P_1 is the value of the same quantity at a point whose temperature has a fixed value, say θ_1 . Since $P \propto n\theta$, the value of σ may also be written

$$\sigma = + \frac{1}{\epsilon} \left\{ \frac{R}{\gamma - 1} - R\theta \frac{\partial}{\partial \theta} \left(\log \frac{n}{n_1} \right) \right\}.$$

This formula differs from those given by both Drude and J. J. Thomson in the articles referred to. In Drude's case the logarithmic term differs by a factor of 2, which arises in the same way as the difference in the expression he finds for the Peltier effect. There also seems to be a confusion of sign in the expression for the heat generated by the internal electric forces. When these changes are made his formula reduces to that of J. J. Thomson. Both writers seem to neglect the energy required to push the electrons against their own pressure as they flow along the unequally heated conductor. The formula which I have found may be deduced after the manner of J. J. Thomson's calculations if this is taken into account. For, consider the electrons present in the region between two isothermal (and also equipotential) surfaces whose temperatures are θ and $\theta + d\theta$ respectively. The internal (kinetic) energy of the electrons on entering at the surface θ is $C_v\theta$, and on leaving at the surface $\theta + d\theta$ is $C_v(\theta + d\theta)$. The work done by the electrons at entrance is $(pv)_\theta = R\theta$, and on the electrons at leaving is

$$(pv)_{\theta+d\theta} = R(\theta + d\theta)$$

The work done on the electrons by the electric forces within the surfaces is

$$R\theta \frac{d}{d\theta} (\log P) d\theta.$$

Thus the net loss of energy by the metal comprised within the surfaces, owing to the passage of this amount of electrons, is

$$\left\{ C_v + R - R\theta \frac{d}{d\theta} (\log P) \right\} d\theta,$$

so that

$$\sigma = + \frac{1}{\epsilon} \left\{ \frac{R\gamma}{\gamma - 1} - R\theta \frac{d}{d\theta} \left(\log \frac{P}{P_1} \right) \right\},$$

in agreement with the previous result.

The value of γ lies between $1\frac{2}{3}$ and 1, so that the minimum value of the first term on the right-hand side is

readily calculated. This minimum value is in every case greater, and in nearly all cases much greater, than the measured values of σ . Thus it follows, as J. J. Thomson has already pointed out, that the two terms must be nearly equal to one another. If the electrons have no internal momentoids $\gamma = 1\frac{2}{3}$, and it is necessary that n the number of free electrons inside a metal should for most metals be nearly proportional to $\theta^{3/2}$. If, on the other hand, $\gamma = 1\frac{1}{3}$, which is another possibility, we should have to have $n \propto \theta^3$ nearly.

An expression * for σ equivalent to the above has been deduced by H. A. Lorentz, on the assumption that the colliding electrons behave like hard elastic spheres.

Thermoelectric Circuits.

Now return to the four conductors AA' B and B', of which A and A' are of the same material, as also are B and B', but the material nature of A and A' is different from that of B and B'. A and B are maintained at the fixed temperature θ_0 , and A' and B' at the fixed temperature θ' . The four conductors are connected together as before. Consider the transportation of a number N of electrons round the circuit thus formed, without leaving the metal. In this case the only work done on balance, if any, is that done against the electrical forces. This is equal to $NT\epsilon$, where T is the thermoelectromotive-force of the circuit. This must be equal to the net absorption of heat during the transference so that

$$NT\epsilon = N\epsilon P' - N\epsilon P + N\epsilon \int_{\theta_0}^{\theta'} \sigma_2 d\theta + N\epsilon \int_{\theta'}^{\theta_0} \sigma_1 d\theta,$$

where P' and P are the Peltier effects at the hot and cold junctions, and σ_2 and σ_1 are the specific heats of electricity in B and A respectively. Substituting the values of P' P σ_2 and σ_1 already obtained we find, after integrating by parts, that

$$T = \frac{R}{\epsilon} \int_{\theta_0}^{\theta'} \log \left(\frac{P_2}{P_1} \right) d\theta = \int_{\theta_0}^{\theta'} \frac{P}{\theta} d\theta,$$

where P_2 and P_1 are the pressures of the free electrons in B and A respectively at the temperature θ , and P is the Peltier effect at a junction formed of A and B at that temperature.

* Quoted by J. Königsberger und J. Weiss, *Ann. der Physik*, vol. xxxv. p. 43 (1911).

Furthermore

$$\frac{dT}{d\theta} = \frac{R}{\epsilon} \log \frac{P_2'}{P_1'} = \frac{P}{\theta'}.$$

Since $P_2 = nR\theta$ and $P_1 = n_1R\theta$, we have

$$\frac{dT}{d\theta} = \frac{R}{\epsilon} \log \frac{n_2}{n_1}.$$

Thus the relative concentrations of the free electrons in different metals may be obtained, at all temperatures, from a knowledge of their thermoelectric powers. Since $\frac{dT}{d\theta}$ is very nearly a linear function of the temperature for most pairs of metals, over a considerable range of temperature, it would seem that n_2/n_1 cannot, for any pair of metals, be represented as a power of θ , but must be of the form $Ae^{b\theta}$, where A and b are constants. This form may, however, only be an empirical approximation.

A theory of thermoelectric phenomena, stated by its author to be based on principles somewhat similar to those which underlie the present development, has just been published in the *Annalen der Physik* by Mr. K. Baedeker*. I am unable to agree with the results of Mr. Baedeker's theoretical calculations, which seem to involve a misconception of the principles which should underlie the applications of the laws of thermodynamics.

The Function w .

The nature of the work w , which an electron has to do in order to escape from a metal, is a matter of considerable interest. If the positive and negative electricity were indefinitely subdivisible, like the mathematical elements of an ideal fluid, then the sign of the work would reverse with the sign of the escaping charge. This follows since, if there were a part of w which did not reverse with the sign of the charge, it would have to depend on the square and other even powers of the latter, and could be made to vanish in comparison with the remainder if the charge were removed in sufficiently small amounts. In such a case w could only arise from a discontinuity in the electric potential at the surface of the conductor, and the natural means of explaining its existence would be to postulate the occurrence of an electrical double layer.

* *Ann. der Phys.* vol. xxxv. p. 75 (1911).

This argument does not apply if the electricity is present in the conductor in the form of electrons. The smallest quantity of electricity which can be removed at one step is finite and equal to the charge of one electron. There is thus always a part of the work done in removing an electron from an uncharged conductor which is proportional to e^2 . This difference between the potential energy of an electron inside and outside the metal may be figured as the work done by the electron against the attraction of its image in the conductor. This is not infinite, as in the ordinary electrostatic theory, because the volume density of the electrification in the ultimate atoms of positive and negative electricity is finite. Sir J. J. Thomson's view that the atoms are spheres of uniformly distributed positive electricity occupied by comparatively small negative electrons of charge e , comparable in number with the atomic weight of the atom, and having an equal total charge, leads to values of w comparable with those given by the results of experiments on the emission of electrons from hot bodies. There is thus no necessity to introduce electrical double layers to account for the existence of the w 's.

This discussion brings out the necessity for using great care in the employment of the terms electric force and electric potential in problems of this character. To obtain the difference of potential between two points A and B it is not sufficient to find the work done in taking an electron from A to B, and to divide the result by the charge e . The quantity thus obtained may differ not only in magnitude but even in sign from the value corresponding to the limit when e is made zero.

The variation of w with θ is a matter of considerable practical interest. If one supposes that the positive electricity in the conductor can be treated as though it were continuously and uniformly distributed throughout its volume, then it appears that w is comparable with e^2/b , where b is the radius of a sphere of the positive electricity which carries a charge e equal to that of the negative electron. From this rough view of the phenomena one would expect that w would diminish with rising temperature, its temperature coefficient being comparable with that of the linear expansion of the material. The experimental data available are inadequate to test this point satisfactorily.

Some further applications of the method which has been developed will be considered in a later paper.

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